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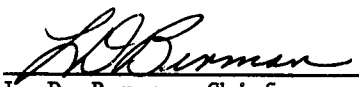
EVALUATION OF THE MECHANISM
OF CORROSION IN CAPILLARIES
STATUS REPORT #1
OXIDIZER DIFFUSION STUDIES
DSR S 11047
ME #531

March 4, 1964

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TEST REPORT

ME NO: 531

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TITLE: Evaluation of the Mechanism of Corrosion in Capillaries.
Status Report #1 - Oxidizer Diffusion Studies

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REFERENCE: DSR S 10447

INTRODUCTION

The evaluation of the mechanism of corrosion in capillaries, being studied, under DSR S 11047, is divided into two major sections: *

- 1) Analytical study of the diffusion characteristics of the storable propellants in water, and vice versa with an experimental program to substantiate the calculated diffusion constants.
- 2) Experimental program to study the actual corrosion in capillaries with various conditions of water with the propellants.

This report consists of the analytical results to date on the diffusion studies on oxidizer - water systems.

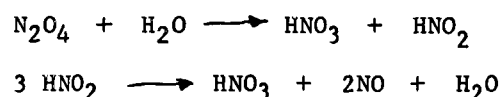
DISCUSSION

Among the mechanisms which have been suggested as possibly contributing to the leakage of the oxidizer, nitrogen tetroxide, from missile tanks are two that involve the generation of the corrosion medium nitric acid in defects such as cracks or pores in the tank wall or along the faying surfaces such as between penetrating fasteners called huckbolts and the tank section. In one of these cases it is postulated that a penetrating pore or capillary below the oxidizer liquid level will, as a result of the positive pressure in the tank or because of capillary forces, become and remain filled with liquid which, initially at least, would be nitrogen tetroxide. This nitrogen tetroxide can absorb moisture from the external atmosphere and produce nitric acid which by corrosion attack on the aluminum alloy capillary wall can lead to an enlargement of the leak path. A second mechanism postulates the formation of nitric acid by reaction of the oxidizer with the water trapped in a crack or leak path as a result of, for example, incomplete drying after hydrostat.

Any mechanism whereby corrosion could take place in a crack or pore in the wall of an oxidizer tank would necessarily involve diffusion of the liquid and gaseous species present as well as the chemical reactions that are known to take place between the oxidizer and water and between the oxidizer hydrolysis products and the tank material.

In the case of the corrosion which might conceivably take place in a water-filled crack or pore below the liquid level in an oxidizer tank, the following reactions appear to be the most important:

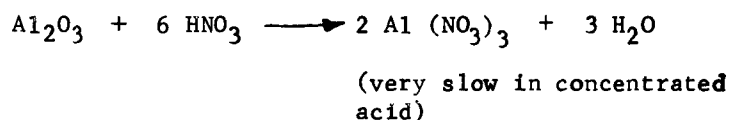
1) hydrolysis of nitrogen tetroxide



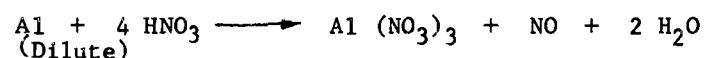
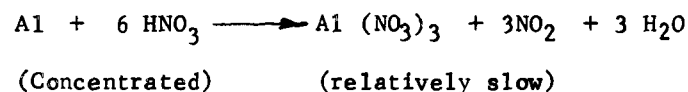
overall reaction



2) dissolution of the air-formed oxide film



3) corrosion attack



To obtain some idea of the relative importance of diffusion on the mechanisms of corrosion in capillaries, diffusion and chemical reaction were arbitrarily separated in a hypothetical case by consideration of the diffusion rate of one of the species, water, assuming no chemical reaction between this diffusing species and the solvent medium, nitrogen tetroxide. A capillary open to the interior of the oxidizer tank is assumed to be filled with water initially and in contact with liquid nitrogen tetroxide as indicated in Figure 1.

As can be seen in the figure the model has been further simplified by being made blind or non-penetrating, and thus eliminating the complication of flow. For a capillary depth of 0.1 inch, which corresponds roughly to the actual tank wall thickness, and assuming a diffusion coefficient of $2 \times 10^{-5} \text{ cm}^2/\text{sec.}$ for water in nitrogen tetroxide, calculation shows that approximately 1 hour could be required for substantially complete removal of water from the capillary by diffusion. This time was computed using the equation:

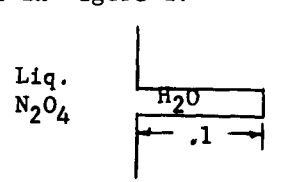


Figure 1

$$C = \frac{4 C_0}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-D (2n+1)^2 \pi^2 t/L^2}$$

C = conc. of H₂O at depth
L at time t

C₀ = initial concn. of H₂O
at L at time t = 0

D = diffusion coefficient of H₂O in N₂O₄
in cm²/sec.

L = capillary depth

which is a solution of Fick's diffusion equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

for the finite linear case.

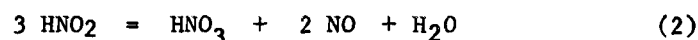
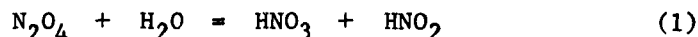
To take into account the effect of the tortuosity of actual cracks and pores as revealed in microphotographs of sectioned weld panels, a second calculation was made for a capillary depth of 0.4 inch. Results indicated that from four to five hours would be required for removal of about 90% of the water from a capillary of this depth (see attached graph).

The significance of the above results lies in the fact that the rate of attack of nitric acid on aluminum and its alloys is strongly dependent on the concentration of the acid or the relative amount of water present. Since the extent of corrosion will be governed by the period of time that the corrosive medium is in contact with the walls of the capillary, the rate of diffusion of water or nitric acid or both out of the capillary is important. The results obtained above using a simplified model suggest, therefore, that the diffusion process will serve to limit the extent of corrosive attack by removal of the corrosive medium in a relatively short time -- a period of several hours or at the most several days.

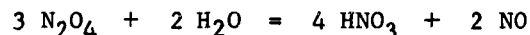
Consideration of the somewhat different case of a water-filled capillary or crack that penetrates the tank wall in the absence of a pressure differential between tank interior and the external atmosphere leads to similar results because of the absence of bulk flow. In this case removal of water from the capillary would be hastened somewhat by some evaporation of water for the condition of low relative humidity of outside atmosphere, while for the opposite extreme of high relative humidity times for removal of the water would approach the values calculated for the blind or non-penetrating capillary.

Treatment of the mechanism of corrosion in a water-filled capillary in contact with liquid nitrogen tetroxide at a somewhat higher level of complexity involves taking into account the reaction of the oxidizer with water to form nitric acid and other products to assess the effect of the reaction on the rates of diffusion of the important reaction products. Larkin has made calculations of this type assuming an instantaneous rate of reaction between nitrogen tetroxide and water. The reaction between N_2O_4 and water is reported to take

place in two steps:



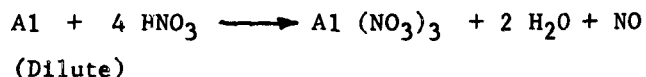
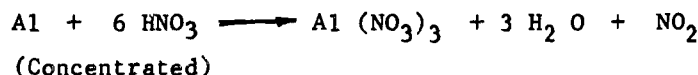
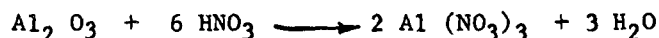
The overall reaction may be written:



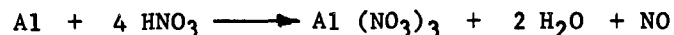
In the interest of simplicity it was assumed that reaction (1), the rate-controlling step, is the only reaction which occurs and further that the reaction of the nitric acid formed with the tank material is slow enough to have negligible effect on the concentration of the diffusing species. Calculations were made of the time required for the moving boundary between the reacting species to reach the back end of a capillary of the type shown in Figure 1 plus the time required for the products of the reaction, HNO_3 and HNO_2 , to diffuse in the opposite direction out of the capillary into the bulk oxidizer into the tank. Results indicated that for a capillary depth of 0.4 inch the total times involved are of the same order of magnitude as for the simpler case treated earlier in which no reaction was assumed. Thus the nitric acid produced by the reaction would be removed from the capillary by diffusion in a relatively short period of time.

If rate data were available for the controlling step in the reaction between nitrogen tetroxide and water, reaction (1) above, the analysis could be carried a step further and a more realistic picture of the concentration profiles of the diffusing species developed. Since the reaction is known to be rapid, however, it appears unlikely that the incorporation of the actual rate data, or some estimate of it based on NO_2 absorption rate data, in the analysis would yield results significantly different from those obtained thus far using simplified approaches.

In the foregoing, the reactions that can take place at the solid-liquid interface in the capillary, i.e., the corrosion reactions have been neglected with the assumption that they were relatively slow compared to the $N_2O_4 - H_2O$ reaction and unlikely to have a great effect on the concentration gradients of the diffusing species. The pertinent corrosion reactions may be summarized as follows:



If we consider the reaction in which nitric acid is formed by the reaction of nitrogen tetroxide with water and one of the corrosion reactions, e.g., that between dilute nitric acid and aluminum



it can be seen that the water consumed in the formation of nitric acid is exactly equal to that produced by the corrosion reaction. This has led to the suggestion that the relatively small amount of water which might be contained initially in a crack or pore in an oxidizer tank wall could conceivably lead to extensive corrosion attack and enlargement of the leak path because of the continuous regeneration of water by the corrosion reaction and the presence of an effectively infinite supply of nitrogen tetroxide. Such a mechanism does not appear likely in view of the results of the diffusion calculations discussed earlier. The continuous formation of nitric acid from the water produced in corrosion requires diffusion to the reaction zone of nitrogen tetroxide as the nitric acid is consumed. Competing with this process, however, is diffusion of water, nitric acid and other reaction products out of the reaction zone into the bulk nitrogen tetroxide. Since the times required for the removal of the diffusion species over the small distances involved in a capillary are relatively short and the corrosion rates relatively slow, it appears unlikely that the contact times involved would be sufficient for extensive corrosion attack to occur.

Estimation of Diffusion Coefficients for Liquids

Values of the diffusion coefficient, D , fall in the range 0.5 to 4×10^{-5} cm^2/sec for a wide variety of solutes and solvents at normal temperatures.

Following are two examples of values reported in the literature:

HNO_3 in H_2O 0.1g- mole/liter 68°F $D = 2.6 \times 10^{-5} \text{ cm}^2/\text{sec}$

CH_3OOOH in H_2O 0.5g- mole/liter 63°F $D = 0.96 \times 10^{-5} \text{ cm}^2/\text{sec}$

D increases with temperature, is larger for small molecules, and decreases usually with the concentration of the solute.

In the absence of experimental values for D , reliable estimates can be made using the empirical equation developed by Wilke and Chang (A.I.Ch.E.J. 1:264 (1955)).

$$D_{12} = 7.4 \times 10^{-8} \frac{(XM)^{\frac{1}{2}} T}{\mu V_1^{0.6}} \quad (1)$$

D_{12} = diffusion of solute (1) in dilute solution of solvent (2) at T , cm^2/sec .

M = mol. wt. of (2)

μ = viscosity of solution, cp.

V_1 = molal volume of (1) at norm b.p., $\text{cm}^3/\text{g. mole}$

X = "association" parameter of solvent

T = $^\circ\text{K}$

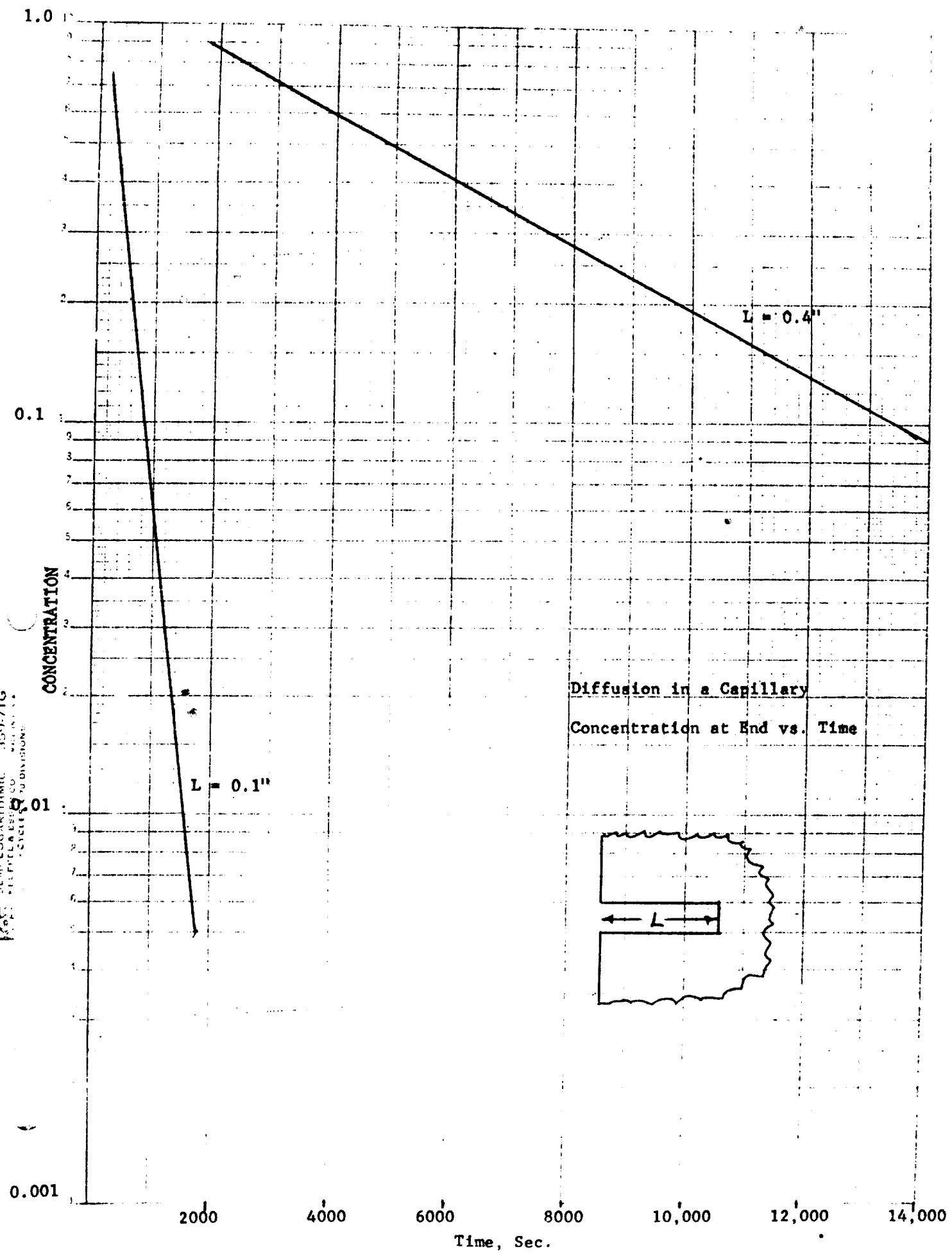
The diffusion coefficient of water in nitrogen tetroxide was estimated using the Wilke-Chang equation and values of 0.413 centipoise for the viscosity of N_2O_4 (1) at 70°F , and $19.4 \text{ cm}^3/\text{g mole}$ for the molal volume of H_2O at its normal boiling point. Since N_2O_4 is a non-polar liquid it is assumed to be non-associated and a value of 1.0 used for X .

Substitution of these values in (1) gives

$$\begin{aligned} D &= 7.4 \times 10^{-8} \frac{(18)^{\frac{1}{2}} (298)}{0.413 \times 19.4^{0.6}} \\ &= 3.84 \times 10^{-5} \text{ cm}^2/\text{sec}. \end{aligned}$$

To allow for possible physical interaction between the water and nitrogen tetroxide and for the effect of increasing concentration of the solute, both of which should reduce D , a value of $2.0 \times 10^{-5} \text{ cm}^2/\text{sec}$. was used for the diffusion coefficient of water in nitrogen tetroxide in the calculations described earlier in this report.

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Diffusion in a Capillary
Concentration at End vs. Time

